

# Formation of Hydrate in Injection of Liquid Carbon Dioxide into a Reservoir Saturated with Methane and Water

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**Abstract**—Injection of liquid carbon dioxide into a depleted natural gas field is investigated. A mathematical model of the process which takes into account forming CO<sub>2</sub> hydrate and methane displacement is suggested. An asymptotic solution of the problem is found in the one-dimensional approximation. It is shown that three injection regimes can exist depending on the parameters. In the case of weak injection, liquid carbon dioxide boils up with formation of carbon-dioxide gas. The intense regime is characterized by formation of CO<sub>2</sub> hydrate or a mixture of CO<sub>2</sub> and CH<sub>4</sub> hydrates. Critical diagrams of the process which determine the parameter ranges of the corresponding regimes are plotted.

*Keywords: gas field, methane, liquid carbon dioxide, injection, hydrate*

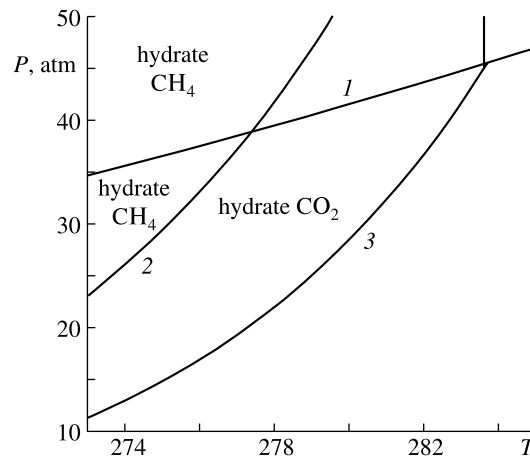
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In recent twenty years considerable attention has been given to minimization of atmospheric emissions and utilization of greenhouse gases leading to global climate change [1]. One of the most abundant greenhouse gases is carbon dioxide. As the prospective technology of CO<sub>2</sub> utilization, its injection into deeply embedded permeable rocks, for example, coal seams [2] or depleted natural gas fields [3], was proposed. In [4, 5] it was suggested to use carbon dioxide injection to intensify methane recovery from the fields containing the gas in the hydrate state.

The problem of leakage due to the high pressure in storing arises in underground utilization of CO<sub>2</sub>. One of the possible solutions of this problem consists in conversion of carbon dioxide into the hydrate state which can be implemented at relatively low temperatures. Then the storing of the same volumes can be implemented at a low pressure. These conditions are present in arctic regions and permafrost areas.

In [6, 7] a mathematical model of carbon dioxide injection into a depleted low-temperature hydrocarbon field containing methane and water in the free state was proposed. Water in the free state interacts with the injected carbon dioxide gas and carbon dioxide hydrate is formed. In this case heat is released and increase in the temperature can be significant. This leads to an undesirable phenomenon, namely, incomplete conversion of gas into hydrate. Consideration is restricted to the low injection pressures ( $\leq 3.5$  MPa) since at the higher pressures carbon dioxide exists in the liquid state.

In the present paper the mathematical model is generalized to include the case of injection of liquid carbon dioxide. The problem is investigated in the self-similar formulation in the one-dimensional approximation. It is shown that, as compared with injection of the gas phase, no significant reservoir heating takes place in the case of injection of liquid carbon dioxide. At the high injection pressures formation of carbon dioxide hydrate on the front can be also accompanied by formation of methane. At the moderate injection rates only CO<sub>2</sub> hydrate is formed, while at the low rates the process is accompanied by boiling of liquid carbon dioxide with formation of the gas phase. Critical diagrams which illustrate the parameter ranges corresponding to three possible regimes of injection of the liquid phase are given.



**Fig. 1.** Domains of existence of methane hydrate and carbon dioxide in the phase plane. Curve 1 is the curve of thermodynamic equilibrium of the liquid and gaseous phases of carbon dioxide and curves 2 and 3 are the curves of dissociation of CH<sub>4</sub> and CO<sub>2</sub> hydrates, respectively. The domains of the stable thermodynamic states of hydrates are located above the curves.

1. FORMULATION OF THE PROBLEM

We will consider injection of liquid carbon dioxide into a homogeneous low-temperature reservoir with the porosity  $\phi$ , the permeability  $k$ , the temperature  $T_0$ , and the pressure  $P_0$ . The reservoir is saturated with a heterogeneous mixture of methane and water in the free state. The conditions of existence of the components are so that the point  $(T_0, P_0)$  in the Clausius–Clapeyron phase plane (Fig. 1) lies below the curve 2 of methane hydrate dissociation and the point  $(T_{inj}, P_{inj})$  determined by the injection temperature and pressure lies above the curve 1 separating the liquid and gaseous states of carbon dioxide. We will consider small values of the water saturation  $S_w$  which are not greater than the flow threshold. This makes it possible to consider water to be immobile.

Contacting with water, injected liquid carbon dioxide forms hydrate. As a result, zone 2 saturated with a mixture of carbon dioxide and CO<sub>2</sub> hydrate and separated from zone 1 saturated with methane and water by the hydrate formation surface are formed.

The governing equations which describe the transfer processes in both regions represent the mass and energy conservation laws, the Darcy’s laws for methane in the gas phase and liquid carbon dioxide, the equations of state, and thermodynamic relations. Under the assumption of immobility of hydrate and the matrix of the porous medium the system of equations for both regions takes the form:

$$\begin{aligned}
 \phi \frac{\partial}{\partial t}(1 - S_j)\rho_i + \text{div } \rho_i \mathbf{v}_i &= 0, \quad (\rho C)_i \frac{\partial T}{\partial t} + \rho_i C_p \mathbf{v}_i \cdot \text{grad } T = \lambda_i \Delta T, \\
 \frac{\partial S_j}{\partial t} &= 0, \quad \mathbf{v}_i = -\frac{k f(S_j)}{\mu_i} \text{grad } P, \quad P = \rho_m R_m T, \\
 \rho_c &= \rho_{c0} [1 + \alpha(P - P_0) - \beta(T - T_0)], \\
 \lambda_{1,2} &= \phi(1 - S_j)\lambda_i + \phi S_j \lambda_j + (1 - \phi)\lambda_s, \\
 (\rho C)_{1,2} &= \phi(1 - S_j)\rho_i C_i + \phi S_j \rho_j C_j + (1 - \phi)\rho_s C_s.
 \end{aligned}
 \tag{1.1}$$

Here,  $T$  is the temperature,  $P$  is the pressure,  $S$  is the saturation,  $v$  is the velocity of flow through the porous medium,  $\mu$  is the viscosity,  $\rho$  is the density,  $\lambda$  is the thermal conductivity,  $C$  is the specific heat,  $f$  is the relative phase permeability, and  $\alpha$  and  $\beta$  are the compressibility of liquid carbon dioxide and the thermal expansion coefficient, respectively. The subscripts “ $m$ ” and “ $c$ ” correspond to methane and liquid carbon dioxide, the subscript “ $i$ ” takes the values  $m$  and  $c$  in the zones containing methane and carbon dioxide, and the subscript “ $j$ ” takes the values  $w$  and  $h$  which correspond to water and carbon dioxide hydrate.

The conditions on the hydrate formation surface represent the energy conservation laws and the methane and carbon dioxide mass conservation laws

$$\phi S_h Q_h V_n = -\lambda_1 (\text{grad } T)_{n1} + \lambda_2 (\text{grad } T)_{n2}, \quad (1.2)$$

$$(1 - S_w) V_n = -\frac{k f_m(S_w)}{\phi \mu_m} (\text{grad } P)_{n1}, \quad (1.3)$$

$$\left[ S_h \left( \frac{\rho_c^{ef}}{\rho_c^*} - 1 \right) + 1 \right] V_n = -\frac{k f_c(S_h)}{\phi \mu_c} (\text{grad } P)_{n2}. \quad (1.4)$$

Here,  $V$  is the velocity of the movable boundary of forming carbon dioxide hydrate,  $\rho_c^{ef}$  is the effective density of  $\text{CO}_2$  in hydrate, and  $Q_h$  is the heat evolved in forming hydrate from liquid carbon dioxide and water. The subscript “ $n$ ” and asterisk denote the normal component and the values of quantities on the front. For the sake of simplicity we will assume that the relative phase permeabilities are linear functions.

We note that in the general case the point  $(T_*, P_*)$  in the phase plane (Fig. 1) corresponding to the temperatures and pressures on the  $\text{CO}_2$  hydrate formation surface does not belong to curve 3 but lies above it. This is attributable to the fact that the thermodynamic conditions of existence of carbon dioxide hydrate can be reached in the zone ahead of the front but hydrate cannot be formed due to the absence of liquid carbon dioxide.

We can eliminate the densities and the velocity of components from the system of governing equations (1.1). If the difference between the temperature of injected liquid carbon dioxide and the initial reservoir temperature is much less than the absolute temperature, the energy equation can be linearized. We will assume that the change in pressure in region 1 is small as compared with the initial pressure. Then, neglecting the small terms, we obtain the following system of linear equations for the saturation, the pressure, and the temperature in both regions:

$$\begin{aligned} \frac{\partial S_j}{\partial t} = 0, \quad \frac{\partial P}{\partial t} = \kappa_i \Delta P, \quad \frac{\partial T}{\partial t} = a_i \Delta T \quad (j = w, h, \quad i = 1, 2) \\ \kappa_1 = \frac{k P_0}{\phi \mu_m}, \quad \kappa_2 = \frac{k}{\phi \alpha \mu_c}, \quad a_i = \frac{\lambda_i}{(\rho C)_i}. \end{aligned} \quad (1.5)$$

Using the small compressibility of the liquid phase in region 2, we can simplify the equation for the pressure in the system (1.5) [8]. The term in the left-hand side of the equation is of the order of  $\delta P/t_x$ , where  $\delta P$  is the variation of pressure and  $t_x$  is the characteristic time. Similarly, the right-hand side is of the order of  $k \delta P / \phi \mu_c \alpha L_p^2$ , where  $L_p$  is the characteristic dimension. Then the ratio of the left-hand to the right-hand side is equal to  $\varepsilon = \phi \mu_c \alpha L_p^2 / k t_x$ . From relations on the interface surface (1.4) it follows that  $L_p^2 / t_x \sim k \delta P / \phi \mu_c$ . Combining two last expressions, we obtain  $\varepsilon = \alpha \delta P \ll 1$ . Hence it follows that we can neglect the derivative with respect to time in the equation for the pressure and, as a result, we obtain

$$\Delta P = 0.$$

Thus, the estimates show that the front on which hydrate is forming moves slowly as compared with the pressure redistribution rate in region 2 and the motion in this region is quasi-steady-state.

The formulation of the problem must be supplemented with restrictions of the thermodynamic nature following from the component existence conditions. Firstly, the pressure and the temperature on the interface calculated in the course of solving must correspond to the domain of existence of liquid carbon dioxide. Otherwise, liquid carbon dioxide will evaporate and regions containing gaseous carbon dioxide will be formed. This condition can be expressed by the relation  $P_* > P_{liq}(T_*)$ , where  $P_{liq}(T) = -239.15 + 1.0026T$  is the approximate equation of the curve of carbon dioxide saturation (curve 1 in Fig. 1) which separates the regions of gaseous and liquid phases of  $\text{CO}_2$  in the Clausius–Clapeyron phase plane.

Secondly, the point  $(T_*, P_*)$  corresponding to the quantities on the front must lie below the curve of formation of methane hydrate on the phase plane (curve 2 in Fig. 1) so that the pressure  $P_*$  on the interface is not higher than the pressure  $P_{hm}$  of methane hydrate formation, i.e.,  $P_* < P_{hm}(T_*)$ . Otherwise, a mixture of methane and carbon dioxide hydrates will be formed. The pressure of methane hydrate formation as a function of the temperature can be determined from the relation  $P_{hm} = \exp(49.32 - 9459/T)$ .

Finally, at the low injection rates the temperature of the components on the front can decrease to negative values due to the low temperature of the injected carbon dioxide. This can lead to formation of ice in the physical system.

In these cases the model suggested does not describe the physical process under consideration. Since only the fairly high injection rates are of practical interest, in what follows we will not consider the last restriction.

### 2. SELF-SIMILAR SOLUTION

The basic properties of the process of injection of liquid carbon dioxide into a reservoir with formation of CO<sub>2</sub> hydrate can be illustrated with reference to the self-similar solution for the one-dimensional time-dependent problem. We will assume that at the initial instant of time the reservoir containing methane and water in the free state occupies half-space  $x > 0$  and the initial water saturation, pressure, and temperature are constant

$$t = 0 : S = S_w, \quad P = P_0, \quad T = T_0.$$

At the point  $x = 0$ , which simulates the injection well, the pressure  $P_{inj}$  and the temperature  $T_{inj}$  of injected carbon dioxide are also constant. Then the problem admits the self-similar solution of the form:

$$P = P(\zeta), \quad T = T(\zeta), \quad V(t) = \sqrt{\frac{a_1}{t}}\gamma, \quad \zeta = \frac{x}{2\sqrt{a_1 t}}. \tag{2.1}$$

From the first of the equations of the system (1.5) it follows that in the self-similar approximation the hydrate saturation  $S_h$  is constant in region 2 behind the front. From the H<sub>2</sub>O conservation law and the condition of immobility of water and hydrate we can determine the hydrate saturation behind the front  $S_h = S_w \rho_w / \rho_w^{ef}$ . Hence we can find  $S_h = S_w / 0.784$  when  $\rho_w^{ef} = 784$  and  $\rho_w = 1000 \text{ kg/m}^3$ .

The temperature and pressure distributions can be determined from the expressions

$$\gamma < \zeta < \infty : T(\zeta) = T_0 + (T_* - T_0) \frac{\text{erf}(\zeta)}{\text{erf}(\gamma)}, \quad P(\zeta) = P_0 + (P_* - P_0) \frac{\text{erfc}(\zeta \sqrt{a_1/\kappa_1})}{\text{erfc}(\gamma \sqrt{a_1/\kappa_1})}, \tag{2.2}$$

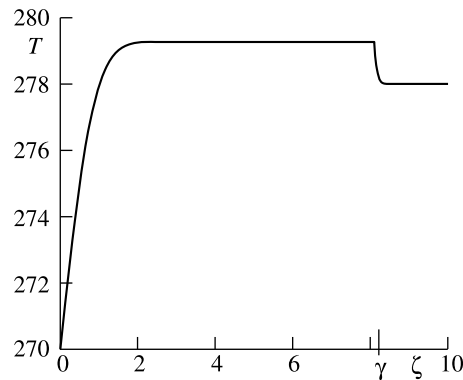
$$0 < \zeta < \gamma : T(\zeta) = T_{inj} + (T_* - T_{inj}) \frac{\text{erfc}(\zeta \sqrt{a_1/a_2})}{\text{erfc}(\gamma \sqrt{a_1/a_2})}, \quad P(\zeta) = P_{inj} + \frac{P_* - P_{inj}}{\gamma} \zeta. \tag{2.3}$$

Substituting the solutions (2.2) and (2.3) in the system of the boundary conditions (1.2)–(1.4), we obtain the system of transcendental equations on the front on which hydrate is forming in dimensionless form:

$$\begin{aligned} \frac{\sqrt{\pi} \phi S_h Q_h a_1}{\lambda_1 T_0} \gamma_1 &= \left( \frac{T_*}{T_0} - 1 \right) \frac{\exp(-\gamma^2)}{\text{erfc}(\gamma)} + \frac{\lambda_2}{\lambda_1} \sqrt{\frac{a_1}{a_2}} \left( \frac{T_*}{T_0} - \frac{T_{inj}}{T_0} \right) \frac{\exp(-\gamma^2 a_1/a_2)}{\text{erf}(\gamma \sqrt{a_1/a_2})}, \\ \gamma &= \sqrt{\frac{\kappa_1}{\pi a_1}} \left( \frac{P_*}{P_0} - 1 \right) \frac{\exp(-\gamma^2 a_1/\kappa_1)}{\text{erfc}(\gamma \sqrt{a_1/\kappa_1})}, \\ \left[ S_h \left( \frac{\rho_c^{ef}}{\rho_c^*} - 1 \right) + 1 \right] \gamma &= -\frac{\kappa}{2a_1} \frac{1 - S_h}{\gamma} \left( \frac{P_*}{P_0} - \frac{P_{inj}}{P_0} \right), \quad \kappa = \frac{kP_0}{\phi \mu_c}. \end{aligned} \tag{2.4}$$

In the system of transcendental equations (2.4) the unknown parameters are the self-similar velocity  $\gamma$ , the temperature  $T_*$ , and the pressure  $P_*$  on the surface on which hydrate is forming.

The system (2.4) was investigated numerically for the following values of the parameters:  $Q_h = 9.6 \times 10^6 \text{ J/m}^3$ ,  $\rho_c^{ef} = 316 \text{ kg/m}^3$ ,  $\rho_h = 1100 \text{ kg/m}^3$ ,  $\rho_s = 2 \times 10^3 \text{ kg/m}^3$ ,  $\mu_m = 1.12 \times 10^{-5} \text{ Pa s}$ ,  $\mu_c = 10^{-4} \text{ Pa s}$ ,  $\lambda_w = 0.58 \text{ W/(m K)}$ ,  $\lambda_s = 2 \text{ W/(m K)}$ ,  $\lambda_h = 2.11 \text{ W/(m K)}$ ,  $C_w = 4.2 \times 10^3 \text{ J/(kg K)}$ ,  $C_s = 10^3 \text{ J/(kg K)}$ , and  $C_h = 2.5 \times 10^3 \text{ J/(kg K)}$ .



**Fig. 2.** Temperature distribution in injection of liquid carbon dioxide and formation of hydrate for  $\phi = 0.2$ ,  $k = 10^{-15} \text{ m}^2$ ,  $S_w = 0.25$ ,  $T_0 = 278 \text{ K}$ ,  $T_{inj} = 270 \text{ K}$ ,  $P_0 = 3.3 \text{ MPa}$ , and  $P_{inj} = 7 \text{ MPa}$ .

### 3. CALCULATION RESULTS

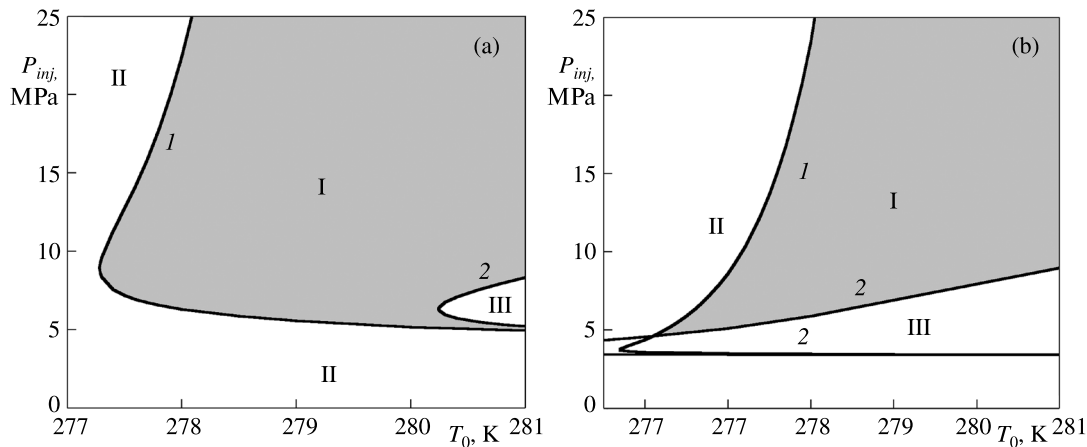
When  $\text{CO}_2$  is injected into a reservoir the pressure varies monotonically decreasing from the injection well, while the temperature reaches a maximum on the interface. In Fig. 2 we have reproduced the characteristic temperature distribution for high injection rates. The increase in the temperature on the front is associated with heat emission due to forming hydrate; however, the heat emission is considerably smaller as compared with the case of gaseous carbon dioxide injection [7] since the enthalpy of gas is greater than the enthalpy of liquid carbon dioxide.

At the high injection rates ( $\gamma \gg 1$ ) jump in the temperature from the initial to maximum value depends on the thermophysical parameters and the amount of  $\text{CO}_2$  hydrate formed, i.e., on the porosity and the initial water saturation. In this case the temperature of injected carbon dioxide has no effect on the front temperature. This statement is also valid in taking the convective energy transfer into account since, due to the high heat capacity of the matrix of the porous medium, the velocity of the temperature front determined by convective energy transfer is lower than the velocity of propagation of the front of the liquid phase by an order of the magnitude [8].

As the injection pressure decreases, the front velocity also decreases and at  $\gamma \simeq 1$  a considerable part of the evolved energy disperses ahead of the front due to heat conduction, thus decreasing the temperature in the neighborhood of the front. In the case of weak injection ( $\gamma < 1$ ) the temperature of liquid carbon dioxide injected into the reservoir becomes significant. In this case the convective energy transfer can be neglected due to the low velocity of liquid carbon dioxide.

Formally, the problem has the solution for any values of the parameters; however, as mentioned above, it is possible that the solution obtained does not satisfy the thermodynamic conditions of existence of the components. In Fig. 3a we have reproduced the critical curves determining the domain of existence of the thermodynamically noncontradictory solution in the case of low-permeability rocks.

The critical curve *I*, which consists of two branches merging at the turning point, separates the injection regimes with (domain I) and without (domain II) forming methane hydrate. On the critical curve the pressure on the front is equal to the pressure of forming methane hydrate and the point  $(T_*, P_*)$  lies on the curve of dissociation (curve 2 in Fig. 1). The critical diagram shows that considerable increase in the injection pressure at a fixed initial temperature leads to an increase in the pressure on the interface which is higher than the pressure  $P_m$  of forming methane hydrate. Significant decrease in the injection pressure initiates decrease in the velocity of front and cooling due to injected carbon dioxide initiates formation of methane hydrate. In the first case methane hydrate is formed as a result of increase in the pressure (upper branch) and in the second case as a result of decrease in the temperature (lower branch). Thus, the inner domain I corresponds to the thermodynamically noncontradictory solution, while the parameters of the outer domain II correspond to the regimes with formation of  $\text{CH}_4$  hydrate which cannot be described by the model proposed. In utilization of  $\text{CO}_2$  the transition of methane into the hydrate state is an undesirable phenomenon since in



**Fig. 3.** Effect of permeability on the domain of existence of the solution (hatched domain) for  $\phi = 0.2$ ,  $S_w = 0.25$ ,  $T_{inj} = 260$  K,  $P_0 = 3.3$  MPa: (a) and (b) correspond to  $k = 0.3 \times 10^{-16}$  and  $10^{-15}$  m<sup>2</sup>, respectively; curve 1 is the critical curve which separates domain I of formation of CO<sub>2</sub> hydrate and domain II of formation of a mixture of CH<sub>4</sub> and CO<sub>2</sub> hydrates; curve 2 is the critical curve which bounds domain III of boiling of the liquid carbon dioxide.

this case a smaller amount of carbon hydrate gets fixed in hydrate, methane is incompletely displaced and remains in the reservoir also in the hydrate state.

The critical curve 2 is the curve of transition from the regime of injection of liquid carbon dioxide to the regime of formation of the gas phase and also is two-valued. On this curve the pressure on the displacement front is equal to the pressure of boiling of liquid carbon dioxide and the point  $(T_*, P_*)$  lies on curve 1 (Fig. 1). Here, at the fixed initial reservoir temperature boiling of the liquid CO<sub>2</sub> phase can be prevented by two ways, namely, by increase in the pressure or by decrease in the temperature on the front. On the upper branch of curve 2 the liquid phase is stabilized due to increase in the injection pressure and, correspondingly, the pressure on the front and on the lower branch due to decrease in the front temperature for slow injection. The intermediate values of the injection pressure correspond to the regimes of boiling of the liquid CO<sub>2</sub> phase and are located in the inner domain of curve 2 (domain III). Thus, the thermodynamically noncontradictory regimes of injection of liquid carbon dioxide occupy the hatched part of domain I. In domain III the model proposed cannot be used and formation of gaseous carbon dioxide must be taken into account.

Within the framework of the model proposed it is impossible to give the quantitative description of the role of the gaseous carbon dioxide interlayer developed and estimate its influence on utilization of CO<sub>2</sub>. However, a comparison of the results of injection of gaseous and liquid carbon dioxide shows that in the last case the mass of injected CO<sub>2</sub> is significantly greater. Therefore, it is natural to assume that boiling of liquid carbon dioxide will lead to deceleration of the injection process.

With increase in the permeability (Fig. 3b) the critical curves are deformed and the critical curve 1 is displaced toward the domain of lower temperatures, while the upper branch of the critical curve 2 rises. This is attributable to the fact that in the high-permeability rocks the pressure on the front grows slower due to the more intense methane outflow from the front zone and impedes formation of CH<sub>4</sub> hydrate. On the other hand, the lower pressure on the front facilitates boiling of liquid carbon dioxide; therefore, the parameter domains corresponding to formation of carbon dioxide is extended.

Numerical experiments show that in injection into high-permeability rocks the turning point of curve 2 goes in the low temperature domain and the upper branch is always located above the lower branch of curve 1. Therefore, the domain of existence of the solution is located between the upper branches of curves 1 and 2 and for finding this domain it is sufficient to determine only the location of the upper branches. Since the case of high-permeability rocks is of greater interest, in what follows we will restrict our attention to finding the upper branches of the critical curves.

Figure 4 illustrates the effect of the initial reservoir pressure on the domain of existence of the solution. As the pressure decreases at the same initial temperature, it is necessary to have the higher injection pressure

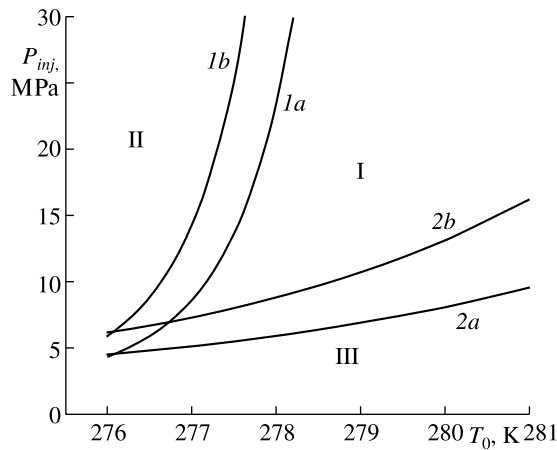


Fig. 4.

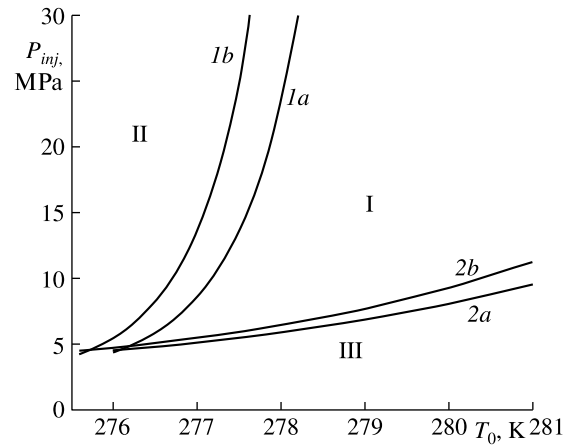
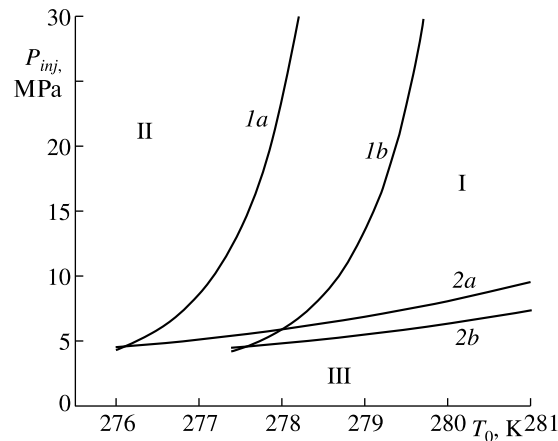


Fig. 5.

**Fig. 4.** Effect of the initial pressure on the domain of existence of the solution. Curves *a* and *b* correspond to  $P_0 = 3.3$  and 3 MPa, respectively. The remaining parameters and the notation are the same as in Fig. 3b.

**Fig. 5.** Effect of the porosity on the domain of existence of the solution. Curves *a* and *b* correspond to  $\phi = 0.2, 0.3$ , respectively. The remaining parameters and the notation are the same as in Fig. 3b.



**Fig. 6.** Effect of the water saturation on the domain of existence of the solution. Curves *a* and *b* correspond to  $S_w = 0.25$  and 0.23, respectively. The remaining parameters and the notation are the same as in Fig. 3b.

to prevent boiling of liquid carbon dioxide. Therefore, the critical curve 2 (Fig. 4) is located considerably higher and the domain of applicability of the model proposed converges. On the other hand, decrease in the initial pressure leads to decrease in the pressure on the front. This prevents formation of methane hydrate and the critical curve 1 rises and the boundaries of applicability of the mathematical model are extended.

Increase in the rock porosity decreases the diffusion coefficient  $\kappa$  and, accordingly, the pressure redistribution rate. In addition, the mass of hydrate formed per unit volume increases and, as a result, the amount of the evolved heat also increases. The influence of the last effect is more significant. This prevents formation of methane hydrate and displaces the point of intersection of the critical curves toward the low temperature domain (Fig. 5). The influence of the porosity on the condition of boiling up of liquid carbon dioxide is less significant; therefore, curve 2 is displaced only slightly.

Decrease in the initial water saturation affects similarly (Fig. 6). On the one hand, the phase permeability increases and, on the other hand, the amount of the heat evolved and the temperature on the front decrease. Therefore, the conditions of formation of methane hydrate become favorable and the critical curve 1 is displaced to the right to the higher temperature domain and reduces significantly the parametric domain of existence of the noncontradictory solution. However, decrease in the temperature prevents boiling of liquid carbon dioxide and curve 2 descends to the low pressure domain and the boundaries of applicability of the mathematical model are extended.

*Summary.* Injection of liquid carbon dioxide into a depleted natural gas field accompanied by forming CO<sub>2</sub> hydrate is considered. It is assumed that initially the reservoir contains methane and water in the free state. Carbon dioxide contacts with water on the front of displacement of residual methane. Under the corresponding thermodynamic conditions this leads to forming carbon dioxide hydrate. A mathematical model of the process is suggested and the one-dimensional problem is investigated in the self-similar approximation.

Calculations show that formation of CO<sub>2</sub> hydrate accompanied by heat evolution leads to increase in the reservoir temperature. Depending on found values of the pressure and temperature on the front, three different injection regimes determined by the thermodynamic state of the components can be implemented. The relatively low pressure on the front leads to phase transition of liquid carbon dioxide into the gaseous state. At the high pressures on the front carbon dioxide hydrate is formed together with methane hydrate. At the moderate pressures liquid carbon dioxide does not boil up and only CO<sub>2</sub> hydrate is formed. The effect of the reservoir parameters and the initial and boundary conditions on the injection regime is investigated. The results are illustrated on the critical diagrams. The mathematical model proposed describes adequately the process only in the last case and it is necessary to modify the model to describe the first two cases.

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